USE INFORMATION AND AIR MONITORING RECOMMENDATIONS FOR THE PESTICIDE ACTIVE INGREDIENTS ACROLEIN

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By
Shifang Fan
Associate Environmental Research Scientist

California Department of
Pesticide Regulation
Environmental Monitoring and
Pest Management Branch

ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM

STATE OF CALIFORNIA
Environmental Protection Agency
Department of Pesticide Regulation
Environmental Monitoring Branch
1001 I Street
Sacramento, California, 95814

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USE INFORMATION AND AIR MONITORING RECOMMENDATION FOR APPLICATION OF THE PESTICIDE ACTIVE INGREDIENT ACROLEIN

A.   BACKGROUND

This recommendation contains general information regarding the physical-chemical properties of acrolein and the reported historical uses as pesticides in California. The Department of Pesticide Regulation (DPR) provides this information to assist the Air Resources Board (ARB) in their selection of appropriate locations for conducting pesticide air monitoring operations.

Physical-Chemical Properties

Acrolein is the simplest member of the class of unsaturated aldehydes. Figure 1 depicts its chemical structure. Acrolein is extremely reactive due to its vinyl group and aldehyde group on such a small molecule (Standen, 1967).

Figure 1   The Chemical Structure of Acrolein
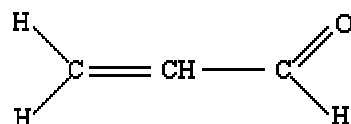
Acrolein is a flammable, colorless to yellowish liquid at room temperature with a piercing, disagreeable, choking odor and extremely acrid. It is soluble in water, alcohol, and ether (Lewis, 1991). Acrolein is unstable. Under light or in contact with alkali or strong acid, it polymerizes to form a plastic solid, disacryl (Windholz, 1976). Table 1 describes some of its physicochemical properties.

Table 1   Some Physicochemical Properties of Acrolein[1]

Chemical name	Acrolein
Common name	Acrolein
Some tradenames[†]	2-propenal, acryl aldehyde, alcrylic aldehyde, aqualin, MagnacideH, Magnacide B
CAS number	107-02-8

[†]Disclaimer: The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

Molecular formula	C_3H_4O
Molecular weight	56.06
Appearance	Clear, colorless liquid
Odor	Aldehydic (extremely irritating)
Vapor pressure (100 °F)	8.6 psia
Vapor pressure (25 °C)[2, 6]	240 – 274 mm Hg
Vapor pressure (20 °C)[3]	29.3 – 36.5 kPa
Vapor density (1 atm)	1.93
Boiling point (1 atm)[3]	52.1 - 53.5 °C
Specific gravity (0 °C)[4]	0.8621
Density (20 °C)[5]	0.8410
Melt point[4]	-88 °C
Freezing point	-124 °F
Flash point	Approx. –20 °F (tag open cup)
	Approx. –13 °F (tag closed cup)
Flammability limits in air	Lower limit 2.8% (by volume)
	Upper limit 31.0% (by volume)
Solubility (20 °C)	Acrolein in water: 22% by weight
	Water in acrolein: 7% by weight
Solubility (25 °C)[3]	206 – 270 g/l
Viscosity (Abs. 32 °F)	0.43 cps
Expansion coefficient (59 °F)	0.000762 per degree F
Henry's Law constant (25 °C)[2]	0.0000745– 0.000192
Henry's Law constant (20 °C)[3]	0.446-19.6 Pa·m^3/mol
Henry's Law constant (25 °C)[3]	7.8 to 180 dimensionless
Octanol-water partition coefficient (Kow)[2]	1.10
Octanol-water partition coefficient (log Kow)[3]	-1.1 – 1.2
Hydration half-lives (25 °C)[2]	0.875 – 3.99 days
Photolysis half-lives (25 °C)[2]	2.22 – 15.4 days
Photolysis half-lives (25 °C)[5]	1.38 days at pH 7.23
	0.875 day at pH 8.87
Soil metabolism half- lives[2]	0.135 – 0.180 day in aerobic conditions
	<1.00 – 18.2 days in anaerobic conditions

Soil adsorption coefficient (Kd)[2]	0.130 – 1.26 depending on soil type, pH, organic carbon content
Soil adsorption coefficient (log Koc)[3]	-0.219 – 2.43

[1]Data from DPR, 2005a except cited elsewhere.
[2]DPR, 2005b
[3]IPCS, 2002
[4]DEH, 2001
[5]Weast, 1975
[6]US EPA, 2003

Acrolein is widely used in chemical industry as an intermediate in the manufacture of various chemical compounds, colloidal metals, plastics, perfumes. Its dimer is used as cross-linking agents for protein collagen, humectants, plasticizers, polyurethane intermediates, copolymers, homopolymers, and crease proofing cotton. The copolymers are used in photography, textile, paper, detergent, and other industries. Acrolein is also directly used for cross-linking protein collagen in leather tanning and tissue fixation in histological samples. The most important direct use of acrolein is as an aquatic biocide for weed, algae, and mollusks control in irrigation system, circulating water process systems, such as cooling-water towers and water treatment ponds. It is also used as a microbiocide in oil wells, liquid hydrocarbon fuels (US EPA, 2005b, OEHHA, 2001).

Environmental Fate Brief

Acrolein is emitted naturally into the atmosphere during animal and plant fermentation metabolic processes and ripening (Eisler, R. 1994), forest fires, and other photochemical oxidation of hydrocarbons in the atmosphere (Ghilarducci & Tjeerdema, 1995). It is released anthropogenically during incomplete combustion of vegetation and synthetic polyethylene plastics, and from waste incinerators, furnaces, fireplaces, power plants, cigarette smoking, and food cooking. The main combustion source is emission from gas and diesel motor vehicles, aircraft, railway engines, ships, and other off-road vehicles (IPCS, 2005). Acrolein can also be formed from breakdown of certain pollutants found in outdoor air (US EPA, 2005a). In general, ambient air concentration of acrolein is higher in urban than rural areas and higher outdoor than indoor air. If acrolein is released to air, with a vapor pressure of 240-274 mm Hg at 25°C it exists solely in its vapor-phase and is degraded in atmosphere by photochemically-produced hydroxyl radicals, ozone, and nitrate radicals with estimated half-lives of 20 hours, 15 days, and 28 days, respectively, for these reactions (US EPA, 2005c). The calculated atmospheric half-life of acrolein, based on rate constants for hydroxyl radical reaction, was between 3.4 and 33.7 hours (Atkinson, 1985; Edney et al., 1986; Haag et al., 1988a; Howard, 1989; BUA, 1994). Acrolein was detected in rainwater, indicating that it might be removed by wet deposition (Grosjean & Wright, 1983). Acrolein in hexane solvent showed moderate absorption of UV light >290nm, which indicated potential for photolytic transformation under environmental conditions (HSDB, 2003). Haag et al. (1988) reported that an observed gas phase photolysis rate constant of 0.063/day yielding a half-life of 10.9 days was comparable to calculated rate constant 0.090/day and half-life of 7.7 days. The overall reactivity-based half-life of acrolein in air was estimated less than 10 hours (Mackay et al., 1995).

Acrolein can enter the aquatic environment by its use as an aquatic herbicide, from industrial discharge, and from the chlorination of organic compounds in wastewater and drinking water treatment (US EPA 2005b). Acrolein is removed from surface water primarily by reversible hydration, biodegradation, and volatilization. Bowmer and Higgins (1976) studied the fate of acrolein in buffered solutions and in natural channel waters. In the buffered solution, an equilibrium between acrolein and its degradation products was reached following dissipation of 92% of the acrolein. The major hydration product was 3-hydroxypropanal. However, acrolein dissipation in natural waters continued to completion. The reaction kinetics study suggested removing the initial degradation products by microbiological processes in natural waters. The half-life of acrolein in natural water was 29 hours compared with 43 hours in thymol-treated water (US EPA 2005c). Calculated hydration half-lives were 1.42 days at pH 7.19 and 0.881 day at pH 8.92 (Haag, et. al., 1988b). Based on Henry's Law constant, volatilization from water surfaces is expected to be an important process. Estimated volatilization half-lives for a model river and a model lake were 4.4 hours and 4.6 days, respectively (US EPA, 2005c). In an earlier study (Bowmer, et al. 1974), an 8- to 10-fold increase in the observed dissipation rate as compared to the expected rate in two of four flowing water channels suggested major losses in volatilization and absorption. However, no aquatic field dissipation studies quantitating the amount of volatilization have been submitted to DPR. Photolysis in natural waters was insignificant with calculated rate of 0.01/day and estimated minimum half-life of 70 days under summer sunlight (Haag et al., 1988a). An estimated bioconcentration factor of 3 suggests the potential for bioconcentration in aquatic organisms is low (HSDB, 2003). Eisler (1994) summarized that when acrolein was applied to irrigation canals to control submerged aquatic weeds, regardless of time-concentration varying from 100 µg/L for 48 hours in the United States to 15,000 µg/L for several hours in Australia, the daily degradation rate constants were remarkably similar, ranging from 0.14 to 0.21, and were probably affected by variations in weed density (O'Loughlin and Bowmer 1975; Parent et al. 1992). In one case, acrolein applied to the Columbia River at an average initial concentration of 125 µg/L and degraded to 25 µg/L after 48 h in samples greater than 65 km from the application point—a loss of 80% (EPA 1980). High initial concentrations (50,000 - 160,000 µg/L) of acrolein in natural waters degraded 57 to 80% in 192 h, suggesting that high concentrations altered the rate of hydrolysis (Kissel et al. 1981). In seawater, the half-life of acrolein was reported less than 20 hours (Rijstenbil and van Galen 1981). IPCS (2005) reports that the overall reactivity-based half-life of acrolein is estimated to be 30–100 hours in surface water and 11–56 days in groundwater. Observed dissipation half-lives of acrolein applied in irrigation canals range from 7.3 to 10.2 hours.

In sediment/water systems, acrolein undergoes hydrolysis, oxidation, and biodegradation. Acrolein is unlikely to bioaccumulate or bioconcentrate significantly in aquatic organisms (IPCS, 2005). Howard et al. (1991) estimated groundwater half-lives of 11 days under aerobic conditions and 14-56 days under anaerobic conditions. In terrestrial environment, acrolein undergoes biodegradation, hydrolysis, volatilization, and irreversible sorption to soil (IPCS, 2005). Haag et al. (1988a) reported that photolysis rate of gas phase acrolein was enhanced twice on a soil surface. However, acrolein partition onto soil surface is small in natural environment and thus photolysis on soil is insignificant. Its absorption by terrestrial plants is poor (IPCS, 2005).

Due to its high vapor pressure and water solubility, acrolein is expected to be highly mobile when released into the environment, although degradation processes are likely to limit its transport (US

EPA, 2005c). The predicted distributions by the Fugacity Modeling suggest that acrolein behaves differently depending on the medium to which it is released and generally, when acrolein is continuously discharged into a specific medium, most of it can be expected to remain in that medium, does not tend to partition from one medium to another. It can also be possible that when acrolein does partition to another medium, its persistence in the second medium is so short that little remains there (IPCS, 2005).

Toxicity Brief

Biochemical and toxic effects of acrolein are caused by its reaction with sulfhydryl compounds to form a stable thiol ether. The main metabolic pathway involves conjugation with glutathione, followed by excretion of mercapturic acid derivatives. Reaction of acrolein with sulfhydryl compounds is rapid and essentially irreversible (Eisler, R. 1994). Acrolein is toxic to cilia in all organisms and interferences with nucleic acid synthesis in bacteria (Marano and Puiseux-Dao 1982; Beauchamp et al. 1985). It destructs vital enzyme systems in plant cells. As a contact herbicide, acrolein eliminates or seriously depletes all populations of aquatic fauna in treated irrigation canals. Terrestrial plants and insects are comparatively resistant to acrolein.   Terrestrial plants tolerated 500 µg/L air and 25,000 µg/L irrigation water; and adult fruit flies (*Drosophila melanogaster*) tolerated 3,700,000 µg/L culture medium. Birds were adversely affected by concentrations greater than 51µg/kg whole egg by injection of eggs, greater than 9,100 µg/kg body weight by single oral doses, and greater than 50,000 µg/L air (Eisler, 1994). Laboratory animals died from inhalation of 8,000-11,000 µg/L after 4-6 hours, mice from 875,000 µg/L after 1 minute and rats from 660 µg/L after 24 days. Animals dying from acute and subacute exposure to acrolein vapor had lung injury with hemorrhagic areas and edema (Albin 1962). Repeated exposures of hamsters, rats, and rabbits to high sublethal concentrations of acrolein caused ocular and nasal irritation, growth depression, and respiratory tract histopathology in all species (Feron and Kruysse 1977). However, repeated exposures to low, tolerated concentrations of acrolein did not produce toxicological effects (Albin 1962), suggesting that acrolein effects are not cumulative and damage can be quickly repaired (Eisler, R. 1994). .

Acrolein is extremely toxic to humans from inhalation and dermal exposure. At low sublethal concentrations, acrolein is strongly irritates on mucous membranes of eyes and of upper respiratory tract. No information is available on its reproductive, developmental, or carcinogenic effects in humans. Two cancer bioassays failed to show an increase in tumor incidence when rats and mice were administered acrolein by gavage. Administration of acrolein in drinking water to female rats resulted in an elevation of adrenocortical tumors over 104-124 weeks, but the increase was only significant when the tumors were combined with hyperplastic nodules. When the data were re-evaluated by an independent pathology working group, the tumors were considered to be well within limits for historical controls and were of no biological significance (US EPA 2005d).

Exposure of general population to acrolein occurs primarily through atmospheric contact. EPA (1993) reported mean ambient acrolein concentrations of 14.3 µg/m^3 (6.2 ppb), ranging from 8.2 to 24.6 µg/m^3 (3.6 to 10.7 ppb) for two urban locations based upon data from 1961 to 1980. IPCS (2002) reported ambient air concentrations are 0.4 µg/m^3, 0.6 µg/m^3, and 1.1 µg/m^3 corresponding to the 90th, 95th, and 99th percentiles of the NAPS data set, respectively. Cigarette smoke,

however, contains about 10,000 µg/L acrolein (Beauchamp et al. 1985). In California, the annual statewide industrial emissions from facilities reporting under the Air Toxics Hot Spots Program were estimated to be 54,565 pounds of acrolein based on the most recent inventory (CARB, 2000; OEHHA, 2001). Occupational exposure to acrolein may occur through inhalation and dermal contact at workplaces. There are currently no tests available to determine personal exposure to acrolein. The half-life of acrolein in drinking water suggests some potential for water to be a source of exposure to humans.

The following health assessment information is summarized from US EPA Integrated Risk Information System (IRIS)'s website http://www.epa.gov/iris/subst/0364.htm (US EPA, 2005c). Since no human studies are available regarding exposure by the oral route, oral reference dose (RfD) is calculated based on mortality as the critical effect in chronic gavage study on the Sprague-Dawley rat (Parent et al., 1992a). The chronic oral RfD is 5×10^{-4} mg/kg-day from the NOAEL 0.05 mg/kg-day multiplies a total uncertainty factor of 100.

Chronic inhalation RfC is 2×10^{-5} mg/m^3 calculated from subchronic rat inhalation study (Feron et al., 1978) with an uncertainty factor of 1000 because no chronic inhalation studies involving human or laboratory animals are available.

The acrolein carcinogen risk was updated and reassessed in 2003. Under the Draft Revised Guidelines for Carcinogen Risk Assessment (U.S. EPA, 1999), the potential carcinogenicity of acrolein cannot be determined because the existing "data are inadequate for an assessment of human carcinogenic potential for either the oral or inhalation route of exposure." No data are available on carcinogenicity in humans exposed solely to acrolein. The only study relating to cancer was a nested case control study by Ott et al. (1989), in which individuals were classified as having been exposed to one of a large number of chemicals in the work environment.

The Cal EPA ranked high in the initial prioritization of Toxic Air Contaminants (TACs) based on research data both in animals *in vivo* and using human tissue *in vitro* strongly suggesting that acrolein may exacerbate asthma, and considering asthma to impact children more than adults. Office of Environmental Health Hazard Assessment (OEHHA 2001) developed acrolein reference exposure levels (REL) for acute and chronic exposure to protect the public from respiratory toxicity. The acute inhalation REL is 0.19 μg/m³ for a 1-hour exposure based on critical effect(s) of eye irritation in healthy human volunteers (OEHHA, 2000).   The chronic inhalation REL is 0.06 μg/m³ (0.03 ppb) based on critical effect(s) of histological changes in nasal epithelium in rats (OEHHA, 2003).

B.   ACROLEIN PESTICIDES USE IN CALIFORNIA

Acrolein as an active ingredient in aquatic herbicides is used to control submersed and floating weeds and algae in irrigation canals, drainage ditches, and irrigation reservoirs. It is injected below the water surface with oxygen-free nitrogen gas.   Because of its high activity against submersed vegetation, concentrations are required in a range of 1-15 ppm (DPR, 2005a). Up to date, two products with 95% acrolein, Magnacide® H Herbicide (acrolein, Inhibited) and Magnacide® B Microbiocide (acrolein, Inhibited), are registered for use in California.

Both herbicide and microbiocide are registered as restricted use pesticides due to high acute toxicity and include the Signal Word "Poison/Danger" on their labels. Their application only conducted by certified applicators or persons under their direct supervision and only for those uses covered by the certified applicator's certification. The application must follow the Application and Safety Manual for application direction, guide, procedures, and safety issues.

Based on the application manual (Baker, 2001), the Magnacide® H Herbicide application dosage (gallons of herbicide per cubic foot per second) is determined depending on the weed growth condition code and water temperature, referring to a weed growth condition chart in the manual. The total amount of herbicide for a canal application is calculated from application dosage multiplying the volume velocity of the water body flow. The acrolein concentration in the water body can be controlled by adjusting the application time. For a given quantity of herbicide to be used and steady water body flow, the shorter the application time, the less water will be treated and the higher acrolein concentration will be in the treated water. While adjusting the application time to achieve a desired concentration, the extend application time must be considered to insure good contact in a fast flowing canal (2 mph or more) application. The herbicide application rate can be calculated from the total quantity of herbicide in gallon divided by the application time in hour. The orifice size and nitrogen pressure setting are determined referring to the Orifice Flow Table on the manual according to the herbicide application rate (gallons per hour). Alternatively, the application rate can be determined by choosing the appropriate application time and concentration based on the weed growth conditions, referring to the table and equations provided on the manual.

Pesticide Use Data Summary

With DPR's implementation of full pesticide use reporting in 1990, all users must report the agricultural use of any pesticide to their county agricultural commissioner, who subsequently forwards this information to DPR. DPR compiles and publishes the use information in the annual Pesticide Use Report (PUR). DPR data for acrolein uses covers applications for rights of way, irrigation systems (ditches, canal banks, etc.), aquatic areas, water areas (all or unspec), aquatic site-industrial use, landscape maintenance, commodity fumigation, uncultivated non-ag areas (all or unspec), structural pest control, public health pest control, vertebrate pest control, regulatory pest control, and crop fumigations.

According to the PUR, the annual use in California from 2000 to 2004 ranged approximately between 290,000 and 211,000 pounds of active ingredient acrolein (Table 2). The majority use of acrolein occurred in four counties- Kern, Stanislaus, Fresno, and Merced. The annual acrolein use of the top four counties accounted for 75% to 85% of the total annual use statewide (Table 2). Table 3 lists monthly use in top four counties for the years of 2000-2004. The high uses in these counties occurred from May to August with the peak use in June and July (Figure 2).

Table 2   Annual Acrolein Use by County (2000-2004)
(Pounds Active Ingredient)

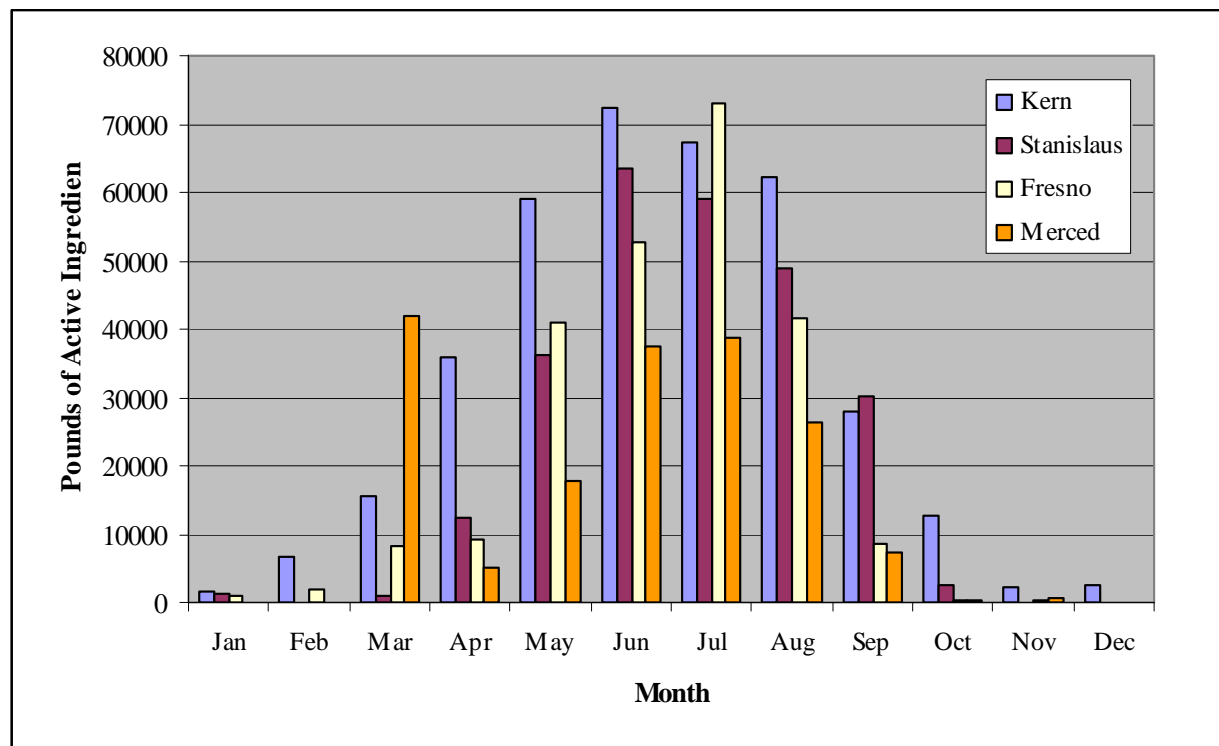| COUNTY	2000	2001	2002	2003	2004	TOTAL
KERN	84525	57636	79808	67338	77092	366398
STANISLAUS	58503	38459	60479	54455	43121	255017
FRESNO	64723	46039	45842	48909	32038	237551
MERCED	28435	56737	33260	33262	23830	175525
SISKIYOU	4424	2778	10178	13216	6317	36913
GLENN	4298	9255	12068	9431		35053
CONTRA COSTA	3815	3969	10145	10158	6264	34351
PLACER	5593	3718	4981	3857	4748	22897
SAN JOAQUIN	815		67	13136	3918	17972
NEVADA	3775	4047	3119	3200	3209	17350
MODOC	5603		6790	3298		15691
SOLANO	7928	2753	1568	1917	1253	15420
TEHAMA	2993	3371	6095	1397	1257	15114
KINGS	3489		2983	3748	2581	12801
MADERA	2509	737	1873	1497	1587	8202
COLUSA	1421	670	2034	983		5108
SAN LUIS OBISPO	1420	806	402	823	1306	4758
SHASTA	770	864	891	886	870	4281
RIVERSIDE	803	817	567	161	355	2703
MONTEREY	669	496	282	531	401	2378
YOLO	2326					2326
SANTA BARBARA	51	373	282	462	727	1895
TULARE	332	297				629
YUBA	142	105	141	67	139	594
SUTTER	526					526
SACRAMENTO	123		82			206
VENTURA	132					132
Statewide use	**290180**	**233928**	**283541**	**272733**	**211014**	**1291792**
Top four counties use	**236186**	**198871**	**219388**	**203965**	**176081**	**1034491**
% top four counties to statewide use	**81**	**85**	**77**	**75**	**83**	**80**

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Table 3   Monthly Acrolein Use by Top Four Counties (2000-2004)
(Pounds Active Ingredient)

County Year	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	Total
Kern Total	**1592**	**6796**	**15433**	**36004**	**59021**	**72378**	**67448**	**62324**	**27849**	**12783**	**2279**	**2492**	**366398**
2000	297	2087	3981	8316	13390	16654	16798	14514	3727	3319	1440		96034
2001		1122	3433	6668	11732	15820	12580	6281					84525
2002	1241	1055	2683	8321	14454	14019	15234	12954	7332	2516			57636
2003		1459	1208	3482	10061	12446	10386	14975	8830	3653	839		79808
2004	54	1074	4128	9217	9385	13438	12450	13600	7959	3296		2492	67338
Stanislaus Total	**1398**		**821**	**12365**	**36091**	**63550**	**59148**	**48839**	**30164**	**2641**			**255017**
2000	171		213	2374	11550	13498	11531	10729	7511	926			68326
2001					7608	7995	6201	11865	4534	255			64723
2002	1227		225	5134	3787	17417	12613	11969	7111	997			46039
2003			383	4857	7684	11584	15614	7139	6886	308			45842
2004					5462	13057	13188	7137	4122	154			48909
Fresno Total	**885**	**2024**	**8134**	**9214**	**41062**	**52618**	**72910**	**41565**	**8471**	**468**	**201**		**237551**
2000	228	35	3391	2299	11507	14123	17763	14167	1211				46707
2001	658	879	1627	1098	11973	13657	10276	4988	681		201		58503
2002		614	1102	2588	7048	11352	15720	6854	362	201			38459
2003		496	916	778	7128	6164	18262	10416	4717	34			60479
2004			1097	2451	3406	7321	10890	5140	1500	233			54455
Merced Total			**41778**	**5048**	**17843**	**37445**	**38882**	**26240**	**7307**	**418**	**565**		**175525**
2000			456	1312	3760	8406	5451	8279	517	255			40258
2001			40216	820	2664	3128	4500	3785	940	119	565		28435
2002			156	1410	3404	10731	11097	3018	3401	43			56737
2003			333	469	6103	6440	12323	6022	1573				33260
2004			617	1038	1913	8741	5511	5135	876				33262
Top four Counties	**3875**	**8820**	**66165**	**62630**	**154017**	**225991**	**238387**	**178969**	**73790**	**16310**	**3045**	**2492**	**1034491**

Figure 2   Monthly Acrolein Use in Top Four Counties for the Years 2000-2004

**Table 4a   Acrolein Use by Application Site during Years of 2000-2004
in Top Four Counties**

(Pounds Active Ingredient)

Year	2000	2001	2002	2003	2004	Total	% Total
RIGHTS OF WAY	214257	175150	189801	182778	165817	**927803**	**90**
AQUATIC AREAS, WATER AREAS (ALL OR UNSPEC)	17383	14234	15877	11184	8500	**67178**	**6**
LANDSCAPE MAINTENANCE	2737	3893	13381	10003		**30015**	**3**
STRUCTURAL PEST CONTROL		5594			598	**6192**	**1**
UNCULTIVATED NON-AG AREAS (ALL OR UNSPEC)	1809					**1809**	**0**
AQUATIC SITE-INDUSTRIAL USE (COMBINED SITE)					710	**710**	**0**
ALFALFA (FORAGE-FODDER) (ALFALFA HAY)					456	**456**	**0**
IRRIGATION SYSTEMS (DITCHES, CANAL BANKS, ETC.)			328			**328**	**0**
Total	**236186**	**198871**	**219388**	**203965**	**176081**	**1034491**	**100**

Table 4b   Acrolein Use by Application Site in Top Four Counties (2000-2004)
(Pounds Active Ingredient)

County	Kern	Stanislaus	Fresno	Merced
RIGHTS OF WAY	282396	255017	214865	175525
AQUATIC AREAS, WATER AREAS (ALL OR UNSPEC)	67178			
LANDSCAPE MAINTENANCE	13976		16038	
STRUCTURAL PEST CONTROL			6192	
UNCULTIVATED NON-AG AREAS (ALL OR UNSPEC)	1809			
AQUATIC SITE - INDUSTRIAL USE (COMBINED SITE)	710			
ALFALFA (FORAGE - FODDER) (ALFALFA HAY)			456	
IRRIGATION SYSTEMS (DITCHES, CANAL BANKS, ETC.)	328			
Total	**366398**	**255017**	**237551**	**175525**
% total of statewide use	**28**	**20**	**18**	**14**

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C.   AIR MONITORING RECOMMENDATIONS

Ninety percent of acrolein use during the years of 2000-2004 was for rights of way applications in the top four counties (Table 4a). Actually, in the Stanislaus and Merced counties, all acrolein applications were for rights of way (Table 4b). Most applications to irrigation canals and reservoirs were reported to this category. DPR suggests ARB monitoring will be conducted for a canal application in one of the top four use counties during summer time in 2006.

Based on a preliminary assessment of the toxicology data, DPR requests the target quantitation limit of 0.7 µg /m^3. DPR suggests monitoring target application rate ranging 4-15 ppm, and application time longer than three hours.

The sampling locations must have enough clearance for sampler placement and airflow. Sample intake should be 1.5 to 1.8 meters above ground. At least two sets of 12 – 14 sampling locations, six or seven on each side of the canal, should be downstream of the application site (Figure 3). The first pair of samplers should be directly across from the point of injection and the remaining five pairs of samplers should be 100-120 meters apart in downstream direction. This first set of 12 samplers will be used during the application period. All sampling locations should be 3-10 meters from canal in the lateral direction. If possible, a seventh pair of samplers should be located further from the canal, 10 – 20 meters in the lateral direction. An extra sampler should be collocated at one sampling location and the collocated sample will be collected at this site during each sampling

interval. A second set of 12 samplers should be established further downstream for the post-application period. These should also be separated by 100-120 m and 3-10 m from the canal. At least two background samples should be collected for 18-24 hours duration prior to application.

DPR recommends close coordination with the county agricultural commissioner or the registrant to select the most appropriate sampling sites. If a sampling site is located on a private property, permission from the property owner must be obtained before the monitoring starts.

The start and end of application (injection) should occur during daylight hours. Preferably, the end of injection should occur approximately one hour before sunset. Air samples should be collected before application, during application, and after application according to the following schedule. The post-application samples should be collected at night because concentrations may be higher due to more stable atmospheric conditions.

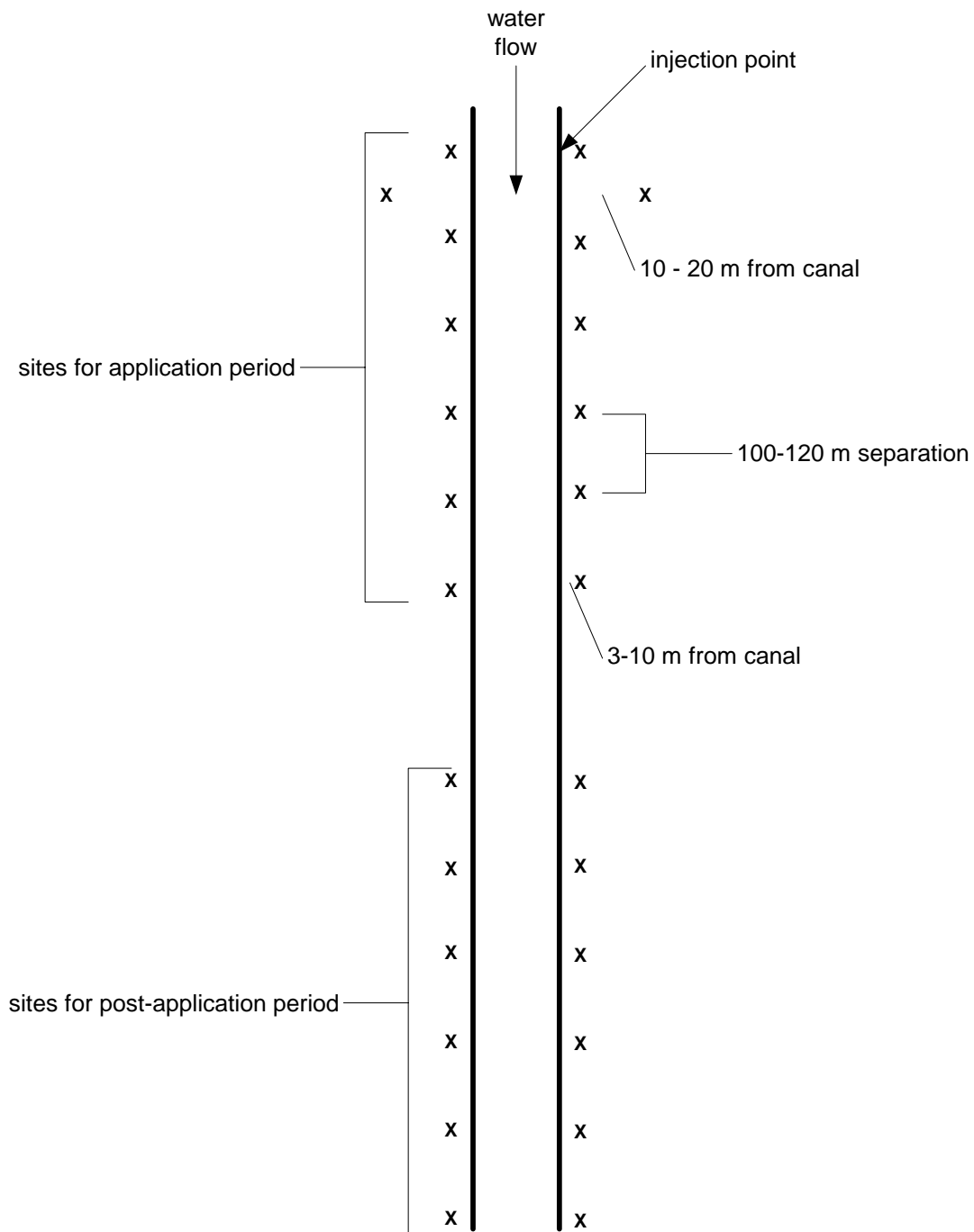| Sample period begins:	Sample duration time
Background (pre-application)	Minimum 18 hours and long enough to meet the recommended ambient quantitation limits
Application (start to end of injection)	4 – 6 hours (day)
Post-application	4 – 6 hours (night)

For quality assurance, trip blanks and field spikes should be prepared in the lab and maintained under the same conditions with the field samples. The field spike level should be 3-60 ppb acrolein.

DPR requests the following information to be included in the monitoring report:

1) an accurate record of the application site, including, but not limited to, topographic features, three dimensions of the water body, water temperature, flow rate, vegetation, and water clearance conditions;
2) an accurate record of the positions of the monitoring equipment, including the exact direction and distance of the samplers, from the application injection point;
3) an accurate record of pesticide application, including application dosage or quantity of pesticide applied, starting and ending time, depth, method, and application rate, etc.
4) an accurate drawing of the monitoring site showing the precise location of the meteorological equipment, trees, other buildings, and other obstacles with respect to North (identified as either true or magnetic North);
5) if applicable, meteorological data collected at 1-minute interval including wind speed and direction, humidity, air temperature, and comments regarding degree of cloud cover.

The applicator should provide most, if not all, of the application information described above.

Figure 3. Sampler layout

water
flow

injection point

x

x

x

x

10 - 20 m from canal

x

x

sites for application period

x

x

100-120 m separation

x

x

x

x

3-10 m from canal

x

x

x

x

x

x

sites for post-application period

x

x

x

x

x

x

D.   SAFETY RECOMMENDATIONS

The following precautions are stated on the Application and Safety manual (Baker, 2001). Most statements pertain to applicators. Therefore, these precautions are reference only for monitoring staff.

Product labels for the acrolein carry a danger/poison warning. Acrolein is extremely flammable. Keep away from fire, sparks, and heated surface. It is poisonous by inhalation, skin contact, or swallowing. Do not breathe vapor. Acrolein is a strong lachrymator. Inhalation of its vapor irritates to eyes, nose, throat and lungs. However, its high lachrymatory activity serves as a warning agent to prevent to unknowingly remain in a vapor contaminated atmosphere long enough to produce serious physiological effects. Acrolein is corrosive and causes eye and skin damage. Do not get in eyes, on skin, or on clothing. The occupational permissible exposure level by OSHA is time weighted average of 0.1 ppm. In case of spill, sodium carbonate (soda ash) powder should be added to the spill and followed dilution by mixing with water.

The manual recommends an applicator must wear a full-face air purifying respirator with organic vapor (OV) cartridges jointly approved by the Mine Safety and Health Administration (MSHA) and the National Institute of Occupational Safety and Health (NIOSH), and butyl rubber gloves. The applicator must also have fresh water available in case of accidental irritation to the eyes or skin and a 10-pound dry chemical fire extinguisher at his disposal. For visual inspection during treatment, chemical splash goggles must be worn.

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